Journal of Photoscience (2002), Vol. 9(3), pp. 51–55

Electronic Spectroscopy and Ligand Field Analysis of *mer*-[Cr(progly)(2,2-tri)]ClO_4

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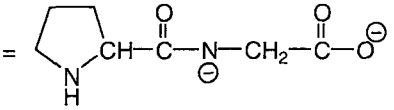
The 77 K emission and excitation spectra, and 298 K infrared and absorption spectra of [Cr(progly)(2,2-tri)]ClO_4 [progly=prolylglycinate, 2,2-tri=N-(2-aminoethyl)-1,2-ethanediamine] have been measured. The vibrational intervals of the electronic ground state are extracted from emission and infrared spectra. The twelve electronic bands due to spin-allowed and spin-forbidden transitions were assigned. Using the observed electronic transitions, a ligand field analysis was performed to determine the metaligand bonding properties for the coordinated atoms. It is found that the carboxylate oxygen of the progly is a strong σ- and π-donor while the peptide nitrogen has weak π-donor property toward chromium(III) ion.

key words: Chromium(III), prolylglycinate, electronic transitions, ligand field properties

INTRODUCTION

In the last few years, the preparations, structural and spectroscopic properties of chromium(III) complexes containing the dipeptides have attracted much attention [1-8]. Coordination behaviors of dipeptides to metal ions are delicately different among metals and peptides. The prolylglycinate (progly) may coordinate to a metal as bidentate or tridentate. Especially, the chromium(III) ion is coordinated via the N(imino), N(peptide) and O(carboxylate) atoms of the prolylglycinate.

progly =



The dipeptides generally form meridionally coordinated complexes as tridentate ligand because the coordinating peptide nitrogen atom is constrained to approximate coplanarity [4]. Thus they can act as strong template ligands to synthesize meridionally coordinated complexes with other tridentate ligands. While the three nitrogens of N-(2-aminoethyl)-1,2-ethanediamine (2,2-tri) are not constrained to planarity, it can adopt both facial and meridional dispositions in coordinating to chromium (III) ion. We have previously reported the synthesis and preliminary spectral properties of the title complex [6]. The application of sharp line electronic spectroscopy to chromium (III) complexes with dipeptide as ligand is a relatively new field that promises to provide an information concerning metal-protein interactions [5-8]. However, an experimental problem lies with the difficulty in distinguish pure electronic components from the vibronic bands that also appear in the sharp-line excitation spectrum.

In this study, the twelve electronic origins due to spin-allowed and spin-forbidden transitions were assigned by analyzing the absorption and excitation spectra. Using the observed electronic transitions, a ligand field analysis was performed to determine the metal-ligand bonding properties for the progly and 2,2-tri ligands toward chromium(III) ion.

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Received July 20, 2002; accepted October 18, 2002

MATERIALS AND METHODS

The L-prolylglycine and N-(2-aminoethyl)-1,2-ethanediamine were purchased from Sigma-Aldrich Chemical Company. All other chemicals were of reagent grade or better quality and used without further purification.

Caution! Although we have experienced no difficulty with the present perchlorate salt, this should be regarded as a potentially explosive compound and treated with care.

The complex [Cr(progly)(2,2-tri)]$ClO_4 \cdot H_2O$ was prepared using previously published method [6]. The compound was recrystallized three times for spectroscopic measurements. *Anal.* Found: C, 30.09; H, 6.01; N, 16.21. Calc. for $Cr(C_{11}H_{23}N_5O_3)ClO_4 \cdot H_2O$: C, 29.84; H, 5.68; N, 15.82.

Analysis for C, H, and N was performed by a Carlo Erba 1108 Elemental Vario EL analyzer. The FT-infrared spectrum was obtained with a Mattson Infinities series FT-IR spectrometer. The room temperature UV-visible absorption spectrum was recorded with a Hewlett-Packard 8453 diode array spectrophotometer. The emission and excitation spectra at 77 K were measured on a Spex Fluorolog-2 spectrofluorometer. The Nitrogen Dewar accessory was used for the low-temperature scan [9,10].

RESULTS AND DISCUSSION

Absorption and IR spectra

The visible absorption spectrum (solid line) of [Cr(progly)(2,2-tri)]$^+$ in aqueous solution at room temperature is represented in Figure 1, including a Gaussian analysis.

It exhibits two bands, one at 20490 cm^{-1} (ν_1) and the other at 27030 cm^{-1} (ν_2), corresponding to the $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}$ (O_h) transitions, respectively [11].

The quartet bands have somewhat asymmetric profiles. In order to have some point of reference for the splittings of the two bands, we have fit the band profiles to four Gaussian curves, as seen in Figure 1. The contribution from outside bands was corrected for fine deconvolution. A deconvolution procedure on the experimental band pattern yielded maxima at 18190, 20980, 25460 and 28015 cm^{-1} for the noncubic split levels of $^4T_{2g}$ and $^4T_{1g}$, respectively. These resolved peak positions were used as the observed spin-allowed transition energies in the ligand field optimization. In fact, using just one Gaussian curve instead of two yields a least squares error only four times that of the best fit (dotted line) shown in Figure 1.

The components of higher energy $^4A_{2g}\rightarrow{}^2T_{2g}$ transition were also found at 20338, 20790 and 21505 cm^{-1} from the second derivative of the solution absorption spectrum, as shown with a dotted line in Figure 2. These components in [Cr(glygly)(3,3-tri)]ClO_4 were observed at 20519, 21008 and 21296 cm^{-1} by using the antiresonance effect due to the close-lying states $^2T_{2g}$ and $^4T_{2g}$ [5].

Figure 3 presents the FT-IR spectrum recorded at room-temperature of [Cr(progly)(2,2-tri)]$ClO_4\cdot H_2O$.

An absorption peak at 3461 cm^{-1} can be assigned to the O-H stretching of H_2O molecule in the hydrate complex. The strong bands in the region of 2800-3300 cm^{-1} are due to the symmetric and antisymmetric N-H and C-H stretching modes. The very strong absorption at 625 cm^{-1} and strong band at

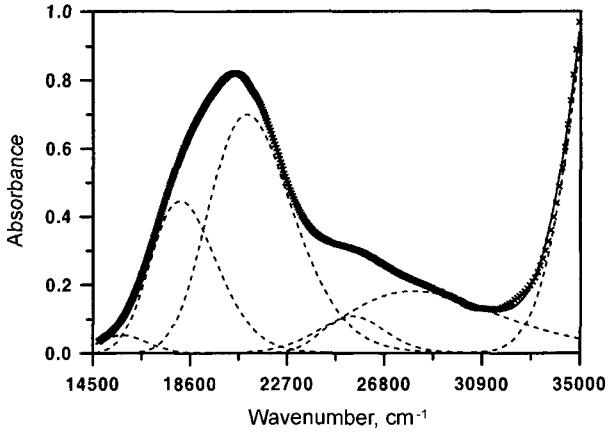

Figure 1. Electronic absorption spectrum of *mer*-[Cr(progly)(2,2-tri)]$^+$ in aqueous solution at 298 K.

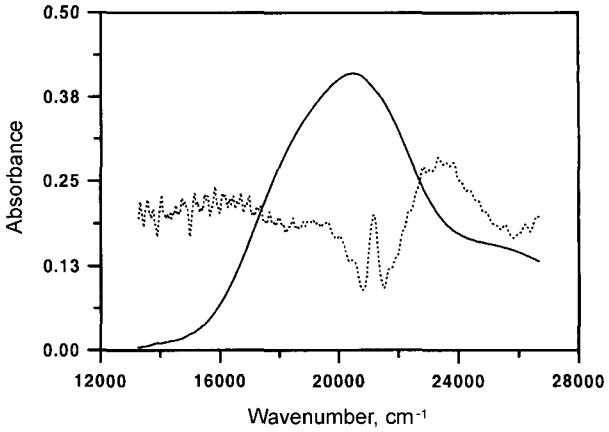

Figure 2. Absorption spectrum (solid line) and second derivative (dotted line) of *mer*-[Cr(progly)(2,2-tri)]$^+$ in aqueous solution at 298 K.

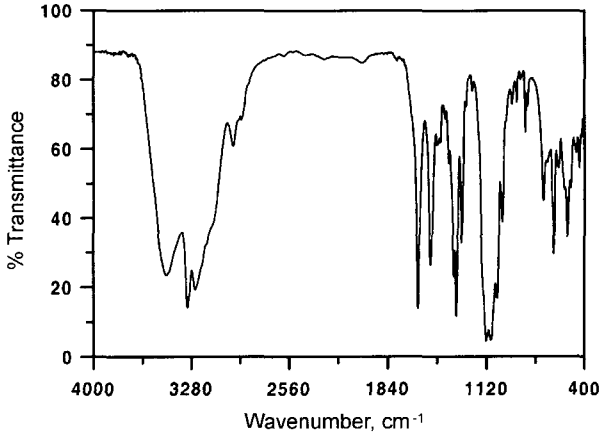

Figure 3. Infrared spectrum of *mer*-[Cr(progly)(2,2-tri)]ClO_4 at 298 K.

1121 cm^{-1} are assigned to ionic perchlorate. The carboxylate stretching frequency of progly is found at 1526 cm^{-1} and peptide carbonyl stretching frequency at 1619 cm^{-1} indicating that both the carboxylate and the deprotonated peptide nitrogen of prolylglyine are coordinated [12]. The infrared spectroscopy is frequently useful in elucidating structures and determining the number of functional groups involved in coordination by a tridentate ligand. In some cases stretching and bending modes of amino groups in metal-amino acid complexes are sensitive to the stereochemistry of the complexes. The CH_2 bending region between 1400 and 1500 cm^{-1} usually consists of three bands for facial isomer, but a single band for meridional isomer. A band near 1260 cm^{-1}, representing a N-H wagging motion, appears for meridional but not for facial isomers, and the NH_2 rocking motions result in one or two bands between 700 and 800 cm^{-1} for facial isomer, but two bands near 850 cm^{-1} for meridional isomer. The N-H wagging mode appears at 1268 cm^{-1} as a medium band. The infrared spectrum of [Cr(progly)(2,2-tri)]$ClO_4\cdot H_2O$ has two NH_2 rocking peaks near 850 cm^{-1} as 834 and 869 cm^{-1}. Another diagnostic band is the N-H stretching

mode near 2900 cm^{-1} for the secondary amine. A peak at 2973 cm^{-1} of medium intensity corresponds to N-H stretching mode of a meridionally coordinated 2,2-tri secondary amine [1]. This intensity band is characteristic of meridional coordination. This assignment is strongly supported by the fact that the configuration of glycylglycinate in [Cr(glygly)(3,3-tri)]ClO_4 was established as meridional geometry by the X-ray structure determination [4].

Emission and excitation spectra

Emission spectrum can be used in addition to infrared spectrum to extract the vibrational intervals of electronic ground state. The 488 nm excited 77 K emission spectrum of [Cr(progly)(2,2-tri)]$ClO_4 \cdot H_2O$ is shown in Figure 4. The

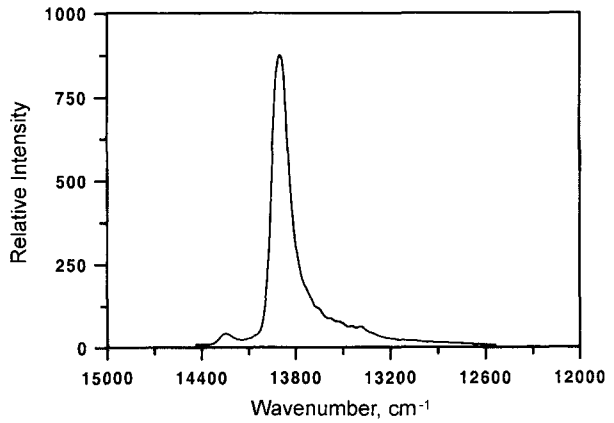

Figure 4. Emission spectrum of *mer*-[Cr(progly)(2,2-tri)]ClO_4 at 77 K (λ_{ex}=488 nm).

Table 1. Vibrational frequencies from the 77 K emission and 298 K infrared spectra for *mer*-[Cr(progly)(2,2-tri)]ClO_4[a]

Emission[b]	Infrared	Assignment
-340 m		R_2
0 vs		R_1
127 m		Lattice vib.,
194 w		skeletal bends
262 w		and ν(Cr-N_p)
321 m		ν(Cr-O)
	419 w	ν(Cr-N)
463 w	436 s, 460 m	
528 w	500 m, 526 vs, 554 w	ν(Cr-N)+Ring def.
	624 vs	ClO_4^-
	672 vw, 701 s	
766 vw	708 m, 735 m,	
855 w	816 m, 834 vs,	
	869 w, 898 m	ρ(NH_2)
963 w	932 m	ρ(CH_2)
	1004 s, 1040 vs	
	1088 vs, 1121vs	

[a]Data in cm^{-1}.

[b]Measured from zero-phonon line at 13895 cm^{-1}.

Table 2. Peak positions in the 77 K sharp-line excitation spectrum of *mer*-[Cr(progly)(2,2-tri)]ClO_4[a]

$\bar{\nu}_0$ - 13866	Assignment	(Calcd)[b]		Vibronic frequencies	Ground state frequencies[c]
0 vs	R_1		ν_1	194	180
183 sh	$R_1+\nu_1$	(180)	ν_2	262	277
270 w	$R_1+\nu_2$	(277)	ν_3	420	423
347 m	R_2		ν_4	463	465
428 sh	$R_1+\nu_3$	(420)	ν_5	528	527
527 ms	$R_2+\nu_1$	(527)			
665 m	672(IR)				
805 s	T_1				
914 m	T_2				
980 vw	$T_1+\nu_1$	(985)			
1091 vs	T_3				
1172 sh	$T_1+2\nu_1$	(1165)			
1217 sh	$T_1+\nu_3$	(1228)			
1272 vw	$T_3+\nu_1$	(1271)			
1327 w	$T_1+\nu_5$	(1332)			
1383 vw	$T_2+\nu_4$	(1379)			
1434 sh	$T_2+\nu_5$	(1441)			
1528 vw	$T_3+\nu_3$	(1514)			
1628 m	$T_3+\nu_5$	(1618)			
1744 w					
1867 w	$T_2+\nu_3+\nu_5$	(1864)			

[a]Data in cm^{-1}.

[b]Values in parentheses represent the calculated frequencies based on the vibrational modes listed.

[c]From the emission and IR spectra (Table 2).

complex exhibits a typical sharp line emission spectrum of $^2E_g \rightarrow {}^4A_{2g}$ (O_h) phosphorescence in chromium(III) complexes. The emission spectrum was independent of the exciting wavelength within the first spin-allowed transition region. The band positions relative to the lowest zero phonon line, with corresponding infrared frequencies, are listed in Table 2.

The strong peak at 13895 cm^{-1} can be assigned to the zero-phonon line, R_1 because a corresponding strong peak is found at 13866 cm^{-1} in the excitation spectrum. A mirror image relationship between the emission and excitation spectra was observed. A well defined hot band at 14235 cm^{-1} may be due to the site effect. The vibrational intervals occurring in the spectrum consist of several modes can be presumed to involve primarily ring torsion and angle-bending modes with frequencies below 280 cm^{-1}. The band at 463 cm^{-1} can be assigned to a Cr-N stretching modes.

The 77 K excitation spectrum is shown in Figure 5. It was recorded by monitoring a relatively strong vibronic peak in the emission spectrum. The spectrum obtained was independent of the vibronic peaks used to monitor it. The peak positions and their assignments are tabulated in Table 3. The calculated frequencies in parentheses were obtained by using the vibrational modes ν_1-ν_5 listed in Table 2.

The sharp peak at 13866 cm^{-1} in the excitation spectrum is

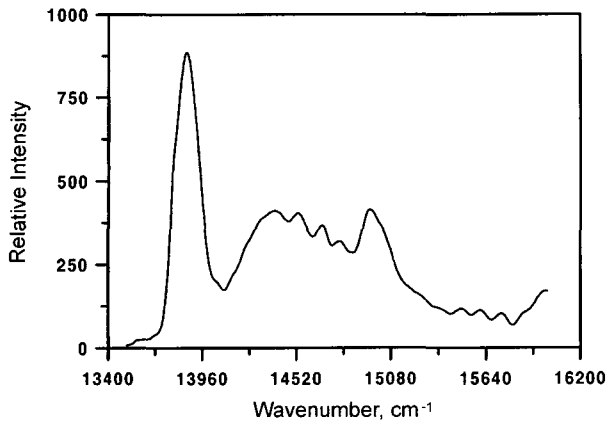

Figure 5. Excitation spectrum of *mer*-[Cr(progly)(2,2-tri)]ClO_4 at 77 K (λ_{em}=750 nm).

Table 3. Experimental and calculated electronic transition energies for *mer*-[Cr(progly)(2,2-tri)]ClO_4[a]

State (O_h)	Exptl	Calcd[b]
^2E_g	13866	13990
	14213	14269
$^2T_{1g}$	14671	14325
	14780	14466
	14957	14828
$^2T_{2g}$	20338	21076
	20790	21640
	21505	22019
$^4T_{2g}$	18190[c]	18618
	20980[c]	20842
$^4T_{1g}$	25460[c]	25921
	28015[c]	27550

[a]Data in cm^{-1}.
[b]e_σ(O)=8032 ± 40, e_π(O)=2104 ± 26, e_σ(N_p)=7350 ± 38, e_π(N_p)=574 ± 8, e_σ(N)=7183 ± 30, B=688 ± 9, C=2755 ± 18, α_T=132 ± 6, ζ=264 ± 8.
[c]Obtained from the Gaussian component deconvolution.

easily assigned to the lowest component (R_1) of the $^4A_{2g}\rightarrow{}^2E_g$ transition. The lowest-energy zero-phonon line coincides with the emission origin within 26 cm^{-1}. A difficulty was experienced in the assignment of the second component (R_2). The medium band at 14213 cm^{-1} is assigned to R_2 line of the $^4A_{2g}\rightarrow{}^2E_g$ transition. The 347 cm^{-1} splitting of the ^2E_g state is larger than the 211 cm^{-1} observed for the [Cr(glygly)(3,3-tri)]ClO_4 complexes [5]. It is also not easy to locate positions of the other electronic components because the vibronic sidebands of the ^2E_g levels overlap with the zero phonon lines of $^2T_{1g}$. However, the three components (T_1, T_2 and T_3) of the $^4A_{2g}\rightarrow{}^2T_{1g}$ electronic origin are assigned to relative intense peaks at 805, 914 and 1091 cm^{-1} from the lowest electronic line, R_1. Vibronic satellites based on these origins have similar frequencies and intensity patterns to those of the ^2E_g components.

Ligand-field calculations

The ligand field analysis was carried out through an optimized fit of experimental to calculated transition energies. The ligand field parameters were calculated using the AOMX program [13]. The doublet and quartet energies with the appropriate degeneracies are calculated by diagonalizing the full 120× 120 secular matrix which arises from the perturbed d^3 system [14]. Eigenvalues were assigned to quartet or doublet states based on a spin analysis of the corresponding eigenfunctions. The amount of quartet character in the doublet states was estimated by comparing the eigenfunctions of the excited doublet states with and without spin-orbit coupling. The ligand field potential matrix was generated for [Cr(progly)(2,2-tri)]ClO_4 from just the six atoms in the first coordination sphere. The crystal structure for any salt of the complex is not solved, thus the positional parameters were adapted from the structure of [Cr(glygly)(3,3-tri)]ClO_4 [4] The coordinates were then rotated so as to maximize the projections of the six-coordinated atoms on the Cartesian axes centered on the chromium. Although the perchlorate oxygens may also perturb the metal d orbitals, the extent of that interaction was judged too small to warrent any additional adjustable parameters. The π-interactions of the carboxylate oxygen and peptide nitrogen with the metal ion were considered to be anisotropic. The π-bonding was described by parallel and perpendicular contributions with respect to the orientation of the π systems of the ligands. For the anistropic ligands of the parameter ratio $e_{\pi\perp}/e_{\pi\parallel}$ was chosen to 0.6 from reasonable values of the corresponding overlap integrals [15]. Since the π-interaction of amine nitrogen with sp^3 hybridization was assumed to be negligible, the nine parameters are involved in the ligand field optimizations. The AOM parameters e_σ(O) and e_π(O) for the carboxylate-chromium interaction, e_σ(N_p) and e_π(N_p) for the peptide-chromium, e_σ(N) for the amine-chromium interaction, plus Racah parameters B, C for the interelectronic repulsion, Trees correction parameter α_T, and the spin-orbit coupling parameter ζ are required to fit thirteen experimental energies: the five $^4A_{2g}\rightarrow\{^2E_g, {}^2T_{1g}\}$ components, identified in Table 3, the three $^4A_{2g}\rightarrow{}^2T_{2g}$ components, the four $^4A_{2g}\rightarrow\{^4T_{2g}, {}^4T_{1g}\}$ components, and the splitting of the ^2E_g state. In order to reduce the parameter space to a minimum, we could use therefore in first approximation parameter values which can be obtained in first good approximation from the quartet band separation ($^4T_{1g}$-$^4T_{2g}\approx 12B$) and from the energy position of lowest doublet term (^2E_g-$^4A_{2g}\approx 9B+3C$). Since the AOM parameters have been found to be transferable between similar compounds, e_σ(N) for the amine nitrogen was well established from calculations on other chromium(III) complexes to have a value around 7300 cm^{-1} [16-19]. We started with the optimization of e_σ and e_π values of the O and N_p ligator atoms, other parameters being assigned to reasonable values. In a second step, all parameters were allowed to vary freely. Racah parameters depend on the value of Trees parameter which is included in the calculations. Finally, we tried to improve the calculated energy level scheme by using a fitting procedure which is based on the Powell parallel subspace algorithm [21].

The results of the optimization and the parameter set used to generate the best-fit energies are listed in Table 3. The quartet terms were given a very low weight to reflect the very large uncertainty in their position [21].

The deduced ligand field parameters are $e_\sigma(O)=8032\pm 40$, $e_\pi(O)=2104\pm 26$, $e_\sigma(N_p)=7350\pm 38$, $e_\pi(N_p)=574\pm 8$, $e_\sigma(N)=7183\pm 30$, $B=688\pm 9$, $C=2755\pm 18$, $a_T=132\pm 6$ and $\zeta=264\pm 8$ cm^{-1}. The AOM parameters are plausible and reproduce the spectrum pretty well. The $e_\sigma(N)$ value for amine nitrogen is located in the normal range. The results for carboxylate oxygen confirm the characterization of the this ligand as a strong σ- and π-donor. The value of the $e_\sigma(N_p)$ is 7350 cm^{-1}, compared with the values for other ligands [22-24]. The positive value of 574 cm^{-1} for $e_\pi(N_p)$ is corresponds to less π-donating ability than carboxylate group. The value of Racah parameter, *B* is about 74% of the value for a free chromium (III) ion in the gas phase. We also can see that the ligand field theory reproduce experimentally observed large splitting of 347 cm^{-1} of $^2E_g(O_h)$ state. An orbital population analysis yields a configuration of $(xy)^{1.018}(xz)^{0.903}(yz)^{1.051}(x^2\text{-}y^2)^{0.009}(z^2)^{0.020}$ for the lowest component of ^2E_g state. The relative *d*-orbital ordering from the calculation is $E(xy)=558$ $cm^{-1}<E(xz)=700$ $cm^{-1}<E(yz)=2160$ $cm^{-1}<E(x^2\text{-}y^2)=21560$ $cm^{-1}<E(z^2)=21799$ cm^{-1}. These factors plus AOM parameters can be used for predicting the photolabilization modes and interpreting the photostereochemistry of the chromium(III) complexes [25]. Since dipeptides are present in biological systems further research ought to be directed towards the possible role of such compounds in biological processes. Meridional coordination at active sites may be possible in reactions catalyzed by metalloenzymes.

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